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## Convenient access to optically active silyl- and germyllithiums: synthesis, absolute structure, and reactivity

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Abstract—A convenient access to optically active silyl- and germyllithium compounds (<sup>*t*</sup>BuMePhELi·sp, E = Si (1), Ge (2)) was accomplished by only addition of (–)-sparteine (abbr. sp) ligand to racemic silyl- and germyllithiums. Optically active silyllithium (1·sp) and germyllithium (2·sp) could be isolated by recrystallization from pentane/toluene mixed solvents. The 1·sp and 2·sp have '*R*' configuration clearly determined by a single crystal X-ray diffraction. Hydrolysis reactions of 1·sp and 2·sp gave the corresponding hydrides, 'BuMePhEH, in quantitative yields with high enantiomeric excess. The reactions of 2·sp with some organic halides were also examined.

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Organic anions, especially those of the group 14 elements (silicon and germanium), have received considerable interest in synthetic chemistry and reaction mechanism.<sup>1</sup> Despite the large number of reports on silyl- or germyllithium reagents, only a limited number of optically active silyl- or germyllithium are known to date. In 1963, Brook pioneered the first preparation of optically active germyllithium compounds by the reaction of enantiomerically enriched hydrogermane with n-butyllithium.<sup>2</sup> On the other hand, optically active silyllithium compounds were first synthesized by Sommer through the cleavage of an Si-Si bond of an enantiomerically enriched disilane with lithium metal.<sup>3</sup> More recently, optically active methyl(1-naphthyl)phenylsilyllithium,<sup>4,5</sup> *n*-butylmethylphenylsilvllithium,<sup>5</sup> and methylphenyl-(1-piperidinylmethyl)silvllithium<sup>6</sup> have been reported. Although there is a variety of synthetic routes to these silyl- and germyllithium compounds, they all require highly enantiomerically enriched hydrosilanes or hydrogermanes as starting material.<sup>7</sup> Moreover, no reports on the isolation of optically active pure silvl- or germyllithium have been published so far, because of the problem of configurational stability of optically active silyl- or germyllithium, which tends to undergo racemization at elevated temperatures due to the loss of

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enantiomerical purity.<sup>8</sup> Herein, we report the direct optical resolution of silyl- and germyllithium compounds by using a chiral ligand of (-)-sparteine (abbr. 'sp') together with their absolute structures and some reactivities.

A racemic mixture of <sup>t</sup>BuMePhGeLi (2) was prepared by the metalation of 'BuMePhGeH with 'BuLi in THF at -40 °C in the presence of half-equivalent of (-)-sparteine. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of a racemic mixture of  $\mathbf{2}$ , single resonances for both <sup>*t*</sup>Bu and Me groups were observed. However, <sup>7</sup>Li NMR showed two resonances at 0.9 and 2.1 ppm with equal intensities, indicating the presence of two different lithium atoms existing in the solution with coordination by THF and (-)-sparteine, respectively. As the temperature was raised, these two signals in <sup>7</sup>Li NMR (in mesitylene- $d_{12}$ ) broadened and disappeared at 380 K, and they finally coalesce to a new signal at 1.5 ppm at 423 K. The temperaturedependent change of the <sup>7</sup>Li NMR signals of 2 may result from the dynamics of exchange of the solvated ligand between two lithium atoms. From the variable temperature <sup>7</sup>Li NMR spectra, the value  $\Delta G^{\ddagger}$ (380 K) = 76 kJ mol<sup>-1</sup> was estimated by the Arrhenius equation for the dynamics of sparteine ligand exchange.9

We have succeeded in the optical resolution of mixture **2** by recrystallization from a toluene/hexane mixed solvent. Only germyllithium **2** with a coordination of (-)-sparteine (**2**·sp) was obtained as colorless crystals in 42% isolated yield.<sup>10</sup> The specific rotation of **2**·sp showed +21.8° in toluene and +16.1° in THF. As

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Scheme 1.

expected, the <sup>7</sup>Li NMR spectrum of  $2 \cdot \text{sp}$  gave one lithium signal at 2.1 ppm. Compound  $2 \cdot \text{sp}$  was *stable* up to 150 °C under argon in the solid state or in dried and degassed hydrocarbon solvents (Scheme 1).

The absolute structure of **2**·sp was unequivocally confirmed by X-ray diffraction (Fig. 1).<sup>11</sup> The crystal structure possesses a monoclinic crystal system and space group of  $P2_1$ , which has no symmetry inversion center. The germanium chiral center has an *R*-configuration. The lithium atom is coordinated by two nitrogen atoms of a (–)-sparteine. The Ge–Li bond length of 2.57(2) Å should be recognized as the shortest one among all solvated germyllithiums hitherto known (2.598(9)– 2.76(2)).<sup>12</sup> The germanium atom has a distorted tetrahedral geometry, which was evidenced by the C–Ge–C bond angles ranging from 99.9(4) to 101.7(3)°. The geometry around the lithium atom is nearly planar with the sum of the bond angles around lithium of  $355(1)^{\circ}$ .

Optical resolution of a silvilithium compound, <sup>*t*</sup>BuMePhSiLi (1), prepared by treatment of disilane, (<sup>*t*</sup>BuMePhSi)<sub>2</sub>, with lithium metal<sup>1</sup> in THF at room tem-



Figure 1. Molecular structure of 2 sp. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge(1)-C(1) 2.029(8), Ge(1)-C(2) 2.045(7), Ge(1)-C(6) 2.045(8), Ge(1)-Li(1) 2.57(2), N(1)-Li(1) 2.04(2), N(2)-Li(1) 2.01(2). Selected bond angles (deg): C(1)-Ge(1)-C(2) 99.9(4), C(1)-Ge(1)-C(6) 101.6(4), C(2)-Ge(1)-C(6) 101.7(3), C(1)-Ge(1)-Li(1) 117.8(4), C(2)-Ge(1)-Li(1) 125.1(4), C(6)-Ge(1)-Li(1) 107.5(4), Ge(1)-Li(1)-N(1) 123.2(5), Ge(1)-Li(1)-N(2) 140.1(6), N(1)-Li(1)-N(2) 91.6(5).

perature by using a chiral ligand of (-)-sparteine was also successful in a similar method.<sup>13</sup> The absolute structure of 1 sp was confirmed by X-ray diffraction. The silicon chiral center has an *R*-configuration.

Hydrolysis reactions of  $1 \cdot \text{sp}$  and  $2 \cdot \text{sp}$  by H<sub>2</sub>O gave the corresponding hydrosilane and hydrogermane in quantitative yields with high enantiomeric excess (92% and 95% ee, respectively). The treatment of  $1 \cdot \text{sp}$  and  $2 \cdot \text{sp}$ by EtOH gave also the corresponding hydrosilane and hydrogermane quantitatively with high enantiomeric excess (93% and 95% ee, respectively). The reactions of optically active germyllithium  $2 \cdot \text{sp}$  with some organic halides in pentane are summarized in Table 1. The reaction of 2·sp with Me<sub>3</sub>SiCl afforded <sup>t</sup>BuMePhGeSiMe<sub>3</sub> in 95% yield. However, the addition of EtBr to 2 sp produced <sup>t</sup>BuMePhGeEt in a lower yield (70%) than that found in the reaction of Me<sub>3</sub>SiCl. Of particular interest is the fact that the reactions of 2 sp with a series of benzylic halides were investigated. On treatment of  $2 \cdot \text{sp}$  with benzyl fluoride, substitution reactions occurred to give the coupling product of <sup>t</sup>BuMePhGeCH<sub>2</sub>Ph in 17% yield with a high enantiomeric excess (96% ee). In this reaction, the formation of 'BuMePhGeH (72%, 95% ee) arising from hydrolysis of unreacted germyllithium was observed due to the short reaction time. On the other hand, the reaction of  $2 \cdot \text{sp}$  with benzyl chloride in pentane produced not only the coupling product <sup>7</sup>BuMePhGeCH<sub>2</sub>Ph (40%, 68% ee) but also <sup>7</sup>BuMePh-GeH (36%) and (<sup>t</sup>BuMePhGe)<sub>2</sub> (trace). Benzyl bromide

Table 1. Reactions of 2 sp with some substrates in pentane

2.sp + substrate $\rightarrow$ product			
1.t., 10 iiiii.			
Substrate	Product	Yield (%) <sup>a</sup>	% ee <sup>b</sup>
H <sub>2</sub> O	<sup>t</sup> BuMePhGeH	100	95
EtOH	<sup>t</sup> BuMePhGeH	100	95
EtBr	<sup>t</sup> BuMePhGeEt	70	
Me <sub>3</sub> SiCl	<sup>t</sup> BuMePhGeSiMe <sub>3</sub>	95	_
PhCH <sub>2</sub> F	<sup>t</sup> BuMePhGeCH <sub>2</sub> Ph	17	96
	<sup>t</sup> BuMePhGeH	72	95
PhCH <sub>2</sub> Cl	<sup>t</sup> BuMePhGeCH <sub>2</sub> Ph	40	68
	<sup>t</sup> BuMePhGeH	36	_
	('BuMePhGe) <sub>2</sub>	Trace	
PhCH <sub>2</sub> Br	<sup>t</sup> BuMePhGeCH <sub>2</sub> Ph	17	23
	<sup>t</sup> BuMePhGeH	15	46
	('BuMePhGe) <sub>2</sub>	Trace	

<sup>a</sup> Determined by GC based on the internal standard of n-C<sub>20</sub>H<sub>42</sub>.

<sup>b</sup> Determined by HPLC using Chiral OJ-H column in hexane/2-propanol (50:1) as an eluent. was reacted with 2·sp to give 'BuMePhGeCH<sub>2</sub>Ph (17%, 23% ee) and 'BuMePhGeH (15%, 46% ee) with a trace amount of ('BuMePhGe)<sub>2</sub>. Although this reaction is not clean and unidentified products were observed, it is noted that the resulting 'BuMePhGeH has small enantiomeric excess, suggesting that the racemization took place in the course of the electron transfer reaction.

We have accomplished a convenient access to optically active silyl- and germyllithiums compounds by only addition of (–)-sparteine ligand. The structure and reactivity of optically active silyl- and germyllithium, and their application to organic synthesis are now under study.

Experimental procedure and NMR spectral data for 1·sp and 2·sp (PDF). X-ray structural data for 1·sp and 2·sp (CIF). These materials are available free of charge via the Internet at http://pubs.acs.org.

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- Typically, enantiomerically enriched silanes or germanes can be prepared by the optical resolution of (-)-menthoxymethyl(1-naphthyl)phenylsilane or germane, see for example: (a) Sommer, L. H.; Frye, C. L. J. Am. Chem. Soc. 1959, 81, 1013; (b) Brook, A. G.; Limburg, W. W. J. Am. Chem. Soc. 1963, 85, 832; (c) Eaborn, C.; Steward, O. W. Proc. Chem. Soc. 1965, 521.
- 8. For example, the optical purity of MeNpPhSiLi in THF at -78 °C keeps 85% ee for 1 h, however, the purity decreased to 50% ee upon raising the temperature up to 0 °C. See Ref. 5.
- 9. The temperature-dependent NMR experiment was performed in mesitylene- $d_{12}$  with a Varian Inova 400 spectrometer (<sup>1</sup>H NMR at 400.0 MHz and <sup>7</sup>Li NMR at 155.4 MHz). No change was observed in the <sup>1</sup>H NMR spectra of **1** at the temperatures ranging from 298 to 423 K.
- 10. Compound 2·sp: mp = 160–161 °C (dec); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 0.68 (s, 3H, Me), 1.42 (s, 9H, 'Bu), 0.5–3.3 (m, 45H, sp), 7.22–7.28 (m, 1H, Ph), 7.40–7.46 (m, 2H, Ph), 7.98–8.02 (m, 2H, Ph); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 0.4 (Me), 18.1, 22.0 (CMe<sub>3</sub>), 24.0, 24.6, 25.0, 25.6, 28.2, 30.2, 31.9 (CMe<sub>3</sub>), 34.8, 35.0, 45.8, 54.3, 57.4, 59.3, 60.6, 66.5, 124.4, 127.0, 135.8, 160.6; <sup>7</sup>Li NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 2.11.
- 11. Crystal structure analysis of (R)-2·sp: Diffraction data were collected at 120 K on a MacScience DIP2030 image plate diffractometer employing graphite-monochromated Mo(K $\alpha$ ) radiation ( $\lambda = 0.71073$  Å); MF = C<sub>26</sub>H<sub>43</sub>-GeLiN<sub>2</sub>, MW = 463.15, monoclinic, P2<sub>1</sub>, a = 10.0640(8), b = 12.9750(9), c = 10.1840(8) Å,  $\beta = 107.659(4)^\circ$ , V =1267.17(17) Å<sup>3</sup>, Z = 2,  $D_{calcd} = 1.214$  g cm<sup>-3</sup>. The final R factor and GOF indicator were 0.0595 (wR2 = 0.1793 for all data) and 1.639, respectively, for 3390 reflections with  $I > 2\sigma(I)$ . The absolute structure parameter converged to 0.00(2). CCDC reference number 194094.
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- 13. Compound 1·sp: mp = 119–120 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 0.68 (s, 3H, Me), 1.42 (s, 9H, <sup>1</sup>Bu), 0.5–3.4 (m, 45H, sp), 7.23–7.28 (m, 1H, Ph), 7.42–7.48 (m, 2H, Ph), 7.97–8.02 (m, 2H, Ph); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 0.9 (Me), 18.0, 19.6 (*C*Me<sub>3</sub>), 23.9, 24.5, 25.0, 25.9, 28.1, 30.3, 31.2 (*CMe*<sub>3</sub>), 34.7, 34.9, 45.8, 54.5, 57.3, 59.3, 60.4, 66.0, 124.7, 126.8, 135.8, 156.6; <sup>7</sup>Li NMR (155 MHz, C<sub>6</sub>D<sub>6</sub>,  $\delta$ ) 1.92.